# ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING

## VOLUME 4

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are generally improved on cross-linking. Among other properties, thermal expansion and heat capacity are lowered, and heat distortion temperature, tensile strength, and refractive index are raised. Glass-transition temperature increases with increasing cross-link density (26). The increase $\Delta T_g$ in glass-transition temperature can be approximated by the following relationship:

$$\Delta T_g = A\nu \qquad (23)$$

where $\nu$ = moles of cross-links per gram of polymer and the constant $A$ is of the order $10^4$–$10^5$. For styrene–divinylbenzene polymerization ($A = 7 \times 10^4$), the elevation in $T_g$ is 12°C for a cross-link density change of $10^{20}$ cross-links per gram of polymer. For natural rubber cross-linked with dicumyl peroxide, $\Delta T_g$ is 6°C for the same change in cross-link density (27).

If a material is cured (cross-linked) isothermally at cure temperature $T_{cure}$, the rise in $T_g$ reduces the chain mobility, and as $T_g$ approaches $T_{cure}$ the reaction may become diffusion controlled and eventually stop as the system undergoes vitrification (28). Complete cure is therefore obtained by curing at a temperature that is above the ultimate glass-transition temperature $T_{g\infty}$ of the system (29). Isothermal time–temperature–transformation (TTT) diagrams may be used to describe the various stages of cure in a thermosetting polymer (see CURING). Figure 5 shows a TTT diagram indicating regions of ungelled glass, liquid, gelled glass, gelled rubber, and char (30). At a very high temperature, the material decomposes to form char. Although the chemical reaction is extremely slow below $T_g$, sufficient reaction can take place over longer periods of time so that upon aging (qv) $T_g$ may rise to 40°C above $T_{cure}$.
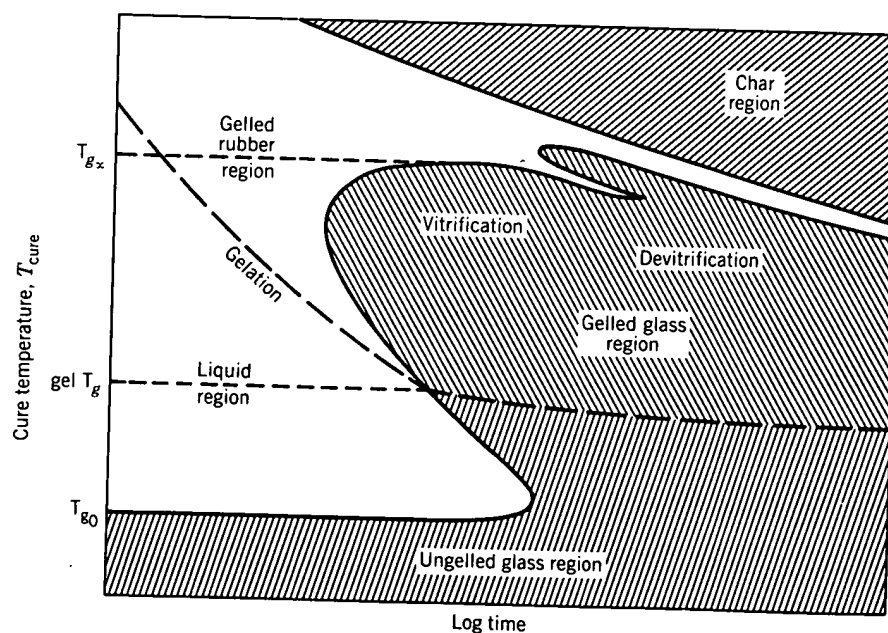


**Fig. 5.**   Time–temperature–transformation (TTT) diagram.